finds in *International Tables for Crystallography*, Volume A. The various $(3+1)$-dimensional superspace groups for each basic group are distinguished by the number m. Furthermore, the symbol of the basic space group, the point group, and the symbol for the corresponding superspace group are given. In the last column, the special reflection conditions are listed for typical symmetry elements. These may help in the structure analysis. The $(2+d)$-dimensional superspace groups, relevant for modulated surface structures, are given in Tables 9.8.3.4(*a*) and (*b*).

9.8.3.5. *Examples*

(*A*) Na_2CO_3

Na_2CO_3 has a phase transition at about 753 K from the hexagonal to the monoclinic phase. At about 633 K, one vibration mode becomes unstable and below the transition temperature $T_i = 633$ K there is a modulated γ-phase (de Wolff & Tuinstra, 1986). At low temperature (128 K), a transition to a commensurate phase has been reported.

The main reflections in the modulated phase belong to a monoclinic lattice, and the satellites to a modulation with wavevector $\mathbf{q} = \alpha\mathbf{a}^* + \gamma\mathbf{c}^*$, b axis unique. The dimension of the modulation is one. The main reflections satisfy the condition

$$hkl0, h + k = \text{even}.$$

Therefore, the lattice of the average structure is C-centred monoclinic. For the satellites, the same general condition holds ($hklm, h + k =$ even). From Table 9.8.3.6, one sees after a change of axes that the Bravais class of the modulated structure is

$$\text{No. 4: } 2/mC(\alpha 0\gamma).$$

Table 9.8.3.2(*a*) shows that the point group of the vector module is $2/m(\bar{1}1)$. The point group of the modulated structure is equal to or a subgroup of this one.

The space group of the average structure determined from the main reflections is $C2/m$ (No. 12 in *International Tables for Crystallography*, Volume A). The superspace group may then be determined from the special reflection condition

$$h0lm, m = \text{even}$$

using Table 9.8.3.5. There are five superspace groups with basic group No. 12. Among them there are two in Bravais class 4. The reflection condition mentioned leads to the group

$$\text{No. } 12.2 = C2/m(\alpha 0\gamma)0s = P^{C2/m}_{\bar{1}\ s}.$$

In principle, the superspace group could be a subgroup of this, but, since the transition normal–incommensurate is of second order, Landau theory predicts that the basic space group is the symmetry group of the unmodulated monoclinic phase, which is $C2/m$.

(*B*) $ThBr_4$

Thorium tetrabromide has an incommensurately modulated phase below $T_i = 95$ K (Currat, Bernard & Delamoye, 1986). Above that temperature, the structure has space group $I4_1/amd$ (No. 141 in *International Tables for Crystallography*, Volume A). At T_i, a mode becomes unstable and a modulated β-phase sets in with modulation wavevector $\gamma\mathbf{c}^*$. The dimension of the modulation is one, consequently.

The main reflections belong to a tetragonal lattice. The general reflection condition is

$$hklm, h + k + l \text{ even}.$$

Looking at Table 9.8.3.6, one finds the Bravais class to be No. $21 = I4/mmm(00\gamma)$. Table 9.8.3.2(*a*) gives $4/mmm(\bar{1}\bar{1}11)$ for the point group of the vector module.

For the determination of the symmetry group of the modulated structure, one has the special reflection conditions

$$hk00, h \text{ even}; \quad hhl0, 2h + l = 4n; \quad (00l0, l = 4n)$$
$$0klm \text{ (and } h0lm\text{) absent for } m = 1.$$

Higher-order satellites have not been observed. The main reflections lead to the basic group $I4_1/amd$. If one generalizes the reflection condition observed for $0klm$ to $0klm$, $m =$ even, the superspace group is found from Table 9.8.3.5 under the groups 141.x as

$$\text{No. } 141.2 = I4_1/amd(00\gamma)s0s0 = P^{I4_1/amd}_{s\ \bar{1}s1}.$$

(*C*) PAMC

Bis(*n*-propylammonium) tetrachloromanganate (PAMC) has several phase transitions. Above about 395 K, it is orthorhombic with space group *Abma*. At T_i, this β-phase goes over into the incommensurately modulated γ-phase (Depmeier, 1986; Kind & Muralt, 1986). The wavevector of the modulation is $\alpha\mathbf{a}^* + \mathbf{c}^*$. Therefore, the dimension of the modulation is one. Interchanging the a and c axes, one sees from Table 9.8.3.2(*a*) that the Bravais class is No. $14 = mmmC(10\gamma)$. In this new setting, the conventional basis of the vector module is $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, and $\gamma\mathbf{c}^*$ and the general reflection condition becomes

$$HKLm, H + K + m = \text{even}.$$

Therefore, if one considers the vector module as the projection of a four-dimensional lattice, the reflection condition corresponds to a $(\frac{1}{2}\frac{1}{2}0\frac{1}{2})$ centring in four dimensions.

The point group of the vector module is $mmm(11\bar{1})$. The basic space group being *Abma* (or *Ccmb* in the new setting), the superspace group follows from Table 9.8.3.5 as

$$\text{No. } 64.3 = Ccmb(10\gamma) = L^{Ccmb}_{11\bar{1}}$$

or, in the original setting

$$\text{No. } 64.3 = Abma(\alpha 01) = N^{Abma}_{\bar{1}11}.$$

No. 64.4 can be excluded because the reflections do not show the special reflection condition $0KLm$, $m =$ even.

9.8.3.6. *Ambiguities in the notation*

The invariant part v_s^o of the translation part v_s of a $(3+1)$-dimensional superspace-group element is uniquely determined by (9.8.3.5). This does not imply that for each element of the point group there is a translation for which the invariant part is unique up to lattice vectors. The reason is that, for a given element R of the point group and given origin, v_s may be changed when R is combined with a three-dimensional lattice translation $w_s = (\mathbf{w}, 0)$. This situation is well known in ordinary three-dimensional crystallography. For example, the twofold rotation $(x, y, z) \rightarrow (-x, z, y)$ in the space group $P4_132$ has according to Volume A of *International Tables for Crystallography* a translation part $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$. Its invariant part is $(0, \frac{1}{2}, \frac{1}{2})$. However, when the translation part is equivalently taken as $(\frac{1}{4}, \frac{3}{4}, -\frac{3}{4})$, the invariant part vanishes. Therefore, in the symbol for that space group, the corresponding generator is given as the rotation '2' and not as the screw axis '2_1'.

The same situation may occur in $3+1$ dimensions. This can be seen very clearly from the definition of τ [equation (9.8.3.8)]. Since $\mathbf{v}$ is only determined modulo a lattice vector, one may add to it a lattice vector that has a non-vanishing product with $\mathbf{q}^r$.

references